

MENU

SEARCH

INDEX

DETAIL

JAPANESE

LEGAL  
STATUS

1 / 1

## PATENT ABSTRACTS OF JAPAN

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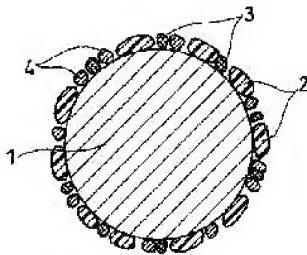
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## (54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the cycle life time of a lithium secondary battery by effectively suppressing problems, such as battery dimensional changes, increase in internal resistance and deterioration of charge and discharge performance with heavy current, resulting from the swelling and contraction of an active material accompanying the charging and discharging of the lithium secondary battery.

SOLUTION: In this lithium secondary battery, the surface of at least one particle of a positive electrode active material and a negative electrode active material is partially covered with a lithium ion conductive polymer. The active material particle surface of the part which is not covered with the polymer is preferably partially or entirely covered with a conductive agent, or the conductive agent and a lithium ion conductive inorganic solid electrolyte.



- 1 活物質粒子
- 2 リチウムイオン伝導性ポリマー
- 3 導電剤

3 導電剤

4 リチウムイオン伝導性無機固体電解質

JAPANESE

[JP,2002-373643,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE  
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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- 3.In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

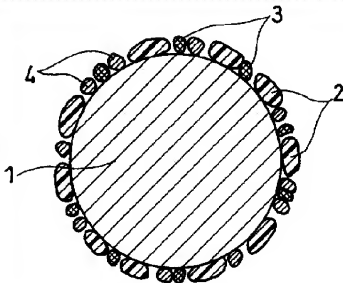
[Claim 1]A lithium secondary battery, wherein the surface of at least one particle of positive active material and negative electrode active material is selectively covered with lithium-ion-conductivity polymer.

[Claim 2]The lithium secondary battery according to claim 1 by which active material particle surfaces other than a portion covered with said lithium-ion-conductivity polymer are covered selectively or extensively by a conducting agent.

[Claim 3]The lithium secondary battery according to claim 1 with which active material particle surfaces other than a portion covered with said lithium-ion-conductivity polymer are covered selectively or extensively by a conducting agent and lithium-ion-conductivity inorganic solid electrolyte.

[Claim 4]Said lithium-ion-conductivity polymer Polyether system resin, polyester system resin, At least one chosen from a group which consists of acrylic resin, polyacrylate system resin, and polyvinylidene fluoride resin, and the lithium secondary battery according to any one of claims 1 to 3 which consists of lithium salt.

Drawing selection **Representative draw**



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[Translation done.]

[Claim 5] Said lithium-ion-conductivity polymer Polyether system resin, polyester system resin, The lithium secondary battery according to any one of claims 1 to 3 which is gel polymer which consists of at least one, lithium salt, and an organic solvent which were chosen from a group which consists of acrylic resin, polyacrylate system resin, and polyvinylidene fluoride resin.

[Claim 6] The lithium secondary battery according to any one of claims 2 to 5 which is at least one chosen from a group which said conducting agent becomes from Ketchen black, acetylene black, black lead, metal powder, metallic coating plastic powder, and metallic coating glass powder.

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[Translation done.]

JAPANESE

[JP,2002-373643,A]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

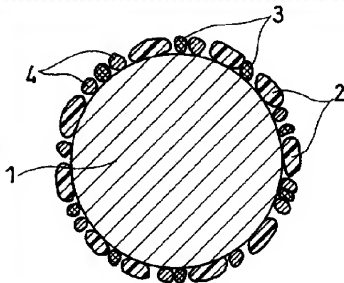
[Field of the Invention]This invention relates to the lithium secondary battery provided with the nonaqueous electrolyte of a liquid, gel, or a solid state.

[0002]

[Description of the Prior Art]In recent years, the demand of the rechargeable batteries as the power supply is very large with the rapid spread of portable devices, such as a personal computer and a cellular phone. Especially a lithium secondary battery is lightweight and attracts attention as a rechargeable battery with which high tension is obtained. Development and utilization of various cells are advanced actively.

The cell using the liquefied organic electrolyte in which the organic solvent was made to dissolve lithium salt among lithium secondary batteries is already completely put in practical use as an object for portable devices, and the cell using a gel polymer electrolyte is also put in practical use partly. There are no worries about a liquid spill and research and development of the lithium secondary battery using

Drawing selection **Representative draw**



- 1 活物質粒子
- 2 リチウムイオン伝導性ポリマー
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[Translation done.]

lithium ion conductivity polymer solid electrolyte or inorganic solid electrolyte are actively done aiming at the cell in which a miniaturization or slimming down is possible.

[0003]Generally, at the time of charge of a lithium secondary battery, negative electrode active material expands, there is a tendency which positive active material contracts, and there is a tendency which the reverse volume change produces at the time of discharge. In the usual charge-and-discharge conditions, as for  $\text{LiCoO}_2$  of positive active material,  $\text{LiMn}_2\text{O}_4$  causes about 3.6% of volume

change 3.2%, for example. In alloy system negative electrodes, such as a TiSn alloy, big cubical expansion happens especially at the time of charge.

[0004]Therefore, in the lithium secondary battery, change of the cell size by charge and discharge, especially expansion of a cell pose a practical big problem. Expansion and contraction of a cell also become the cause of destabilizing contact between electrode-battery containers and increasing the internal resistance of a cell. Since the contact degree between components, such as an active material particle in an electrode, conducting agent particles, and an electrolyte, becomes weaker while an anode and a negative electrode repeat expansion and contraction by a charging and discharging cycle, there is a problem on which the charge-and-discharge performance in a high current deteriorates especially in a lithium secondary battery.

[0005]An inorganic solid electrolyte is made to contain also in an electrode in all the solid lithium secondary batteries which make a lithium-ion-conductivity inorganic solid electrolyte layer intervene between positive and negative poles, and are constituted. Since this inorganic solid electrolyte is hard powder, contact between the particles of an electrolyte and an active material is easy to be severed by expansion and contraction of the electrode by charge and discharge. Thereby, with all the solid lithium secondary batteries, the course of supply of the lithium ion to an active material or discharge is especially intercepted, and there is a problem to which chargeable and dischargeable current falls remarkably.

[0006]In order to solve this problem, all the solid lithium cells which covered the surface of the active material particle with lithium-ion-conductivity polymer are proposed (for example, JP,11-7942,A). This aims at controlling relaxation of junction between the particles by expansion and contraction of the active material in the inside of the electrode at the time of charge and discharge, and the volume change of a cell with the elasticity of said polymer.

[0007]However, since the occupied volume of the polymer

layer within an electrode is large when the surface of an active material particle is extensively covered with a polymer layer as indicated in the example, the volume of the opening formed between the active material particles in an electrode decreases remarkably. Therefore, since polymer of the portion which was compressed at the time of expansion of an active material, and changed is hardly accommodated in said opening but expansion of an active material is reflected in expansion of an electrode as it is, the effect which controls expansion of an electrode is scarce. Since the whole surface of the active material particle is covered with the polymer layer, the network of the electronic conduction between active material particles becomes insufficient, and there is a problem to which a high charging and discharging characteristic falls.

[0008]

[Problem(s) to be Solved by the Invention] This invention solves the problem of the above-mentioned conventional lithium secondary battery, and aims to let degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge-and-discharge performance in a high current provide the lithium secondary battery controlled effectively.

[0009]

[Means for Solving the Problem] As for a lithium secondary battery of this invention, the surface of at least one particle of positive active material and negative electrode active material is selectively covered with lithium-ion-conductivity polymer. As for active material particle surfaces other than a portion covered with said lithium-ion-conductivity polymer, it is preferred to be covered with a conducting agent selectively or extensively. As for active material particle surfaces other than a portion covered with said lithium-ion-conductivity polymer, it is still more preferred to be covered with a conducting agent and a lithium-ion-conductivity inorganic solid electrolyte selectively or extensively.

[0010]

[Embodiment of the Invention] Drawing 1 is a sectional view showing typically the active material particle which carried out coating treatment of the surface by this invention. The surface of the active material particle 1 is selectively covered with the lithium-ion-conductivity polymer 2. If needed, the active material particle surfaces of the portion which is not covered with said polymer 2 are the conducting agent 3 and the lithium-ion-conductivity inorganic solid electrolyte 4, and are covered selectively or extensively.

[0011] The lithium secondary battery of this invention makes it an indispensable condition to cover selectively the surface of the particles of at least one active material of positive active material and negative electrode active material with

lithium-ion-conductivity polymer. Thereby, the lithium secondary battery with which degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge-and-discharge performance in a high current was controlled effectively can be provided.

[0012]In this invention, since the layer of lithium-ion-conductivity polymer has covered the active material particle surface selectively unlike said conventional technology (JP,11-7942,A) and the occupied volume of the polymer layer within an electrode is small, volume of the opening formed between active material particles can be enlarged. When the polymer layer which has pliability is compressed by this at the time of expansion of an active material particle and it changes by it, polymer of the deformed portion can be accommodated in the aforementioned opening. Thus, expansion of an electrode is eased by absorbing expansion of an active material and modification of the polymer layer by it within an electrode.

[0013]At the time of contraction of an active material particle, when the polymer previously transformed by expansion of the active material particle reverts to the original form, change of an electrode size is eased. Thus, the volume change of the cell accompanying charge and discharge is eased, and when storing a cell to the predetermined space especially in apparatus, expansion of the cell which poses a problem can be controlled effectively. The good contact between an electrode and a battery container is maintained simultaneously, and increase of the battery internal resistance by a charging and discharging cycle can be prevented.

[0014]In this invention, since the portions which are not covered with the polymer layer of the surface of an active material particle can be contacted within an electrode, the network of the electronic conduction between active material particles can fully be formed. Since the active material particle is covered by lithium ion conductivity polymer, the course of supply of the lithium ion to an active material particle or discharge is fully secured. By these, the high charging and discharging characteristic of a cell can be raised. The junction nature between each particle in an electrode is strengthened by the binding capacity of the lithium-ion-conductivity polymer covered by the active material particle surface, and even when expansion and contraction of an active material arise at the time of charge and discharge, junction between said particles is maintained. Thereby, the charge-and-discharge cycle life of a cell can be raised further.

[0015]As for the lithium secondary battery of this invention, it is preferred that active material particle surfaces other than the portion covered with lithium-ion-conductivity



polymer are covered with the conducting agent selectively or extensively. By covering an active material particle surface with a conducting agent, the electron conductivity between active material particles can be raised. Thereby, the internal resistance of a cell can be reduced further and the charge-and-discharge performance in a high current can be raised further.

[0016]As for the lithium secondary battery of this invention, it is still more preferred that active material particle surfaces other than the portion covered with lithium-ion-conductivity polymer are covered with the conducting agent and the lithium-ion-conductivity inorganic solid electrolyte selectively or extensively. The usual lithium ion inorganic solid electrolyte is provided with the ionic conductivity of  $10^{-4}$  higher figures double [1-] than lithium-ion-conductivity polymer of a solid state -  $10^{-5}\omega\text{cm}^{-1}$  and cm. Thus, by making an inorganic solid electrolyte with high ionic conductivity adhere to an active material particle surface, the ion conductivity of the active material particle surface selectively covered with lithium-ion-conductivity polymer can be improved further. The effect of the conducting agent which raises the electron conductivity between active material particles can be added to this, and the charge-and-discharge performance in a high current can be raised further.

[0017]Generally, the ionic conductivity of lithium-ion-conductivity polymer of the thing of a solid state is as low as  $10^{-5}$  -  $10^{-6}\omega\text{cm}^{-1}$ , and cm, and a gel thing shows  $10^{-3}$  -  $10^{-4}\omega\text{cm}^{-1}$  and cm, and a high value. Therefore, when polymer of the solid state whose ionic conductivity is comparatively low is used as lithium-ion-conductivity polymer, it is effective to use an inorganic solid electrolyte together as mentioned above in order to raise the ionic conductivity of an active material surface. When this method is applied to all the solid lithium secondary batteries, a big effect is acquired especially.

[0018]As lithium-ion-conductivity polymer of this invention, Polyester system resin, such as polyether system resin, such as polyethylene oxide, and polyester terephthalate, Acrylic resin, acrylonitrile, and acrylonitrile series resin, such as a vinyl acetate copolymer, To and at least one resin chosen from the group which consists of polyvinylidene fluoride resin. Polymer of the solid state in which lithium salt, such as  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ , and  $\text{LiClO}_4$ , was included can be used.

[0019]The following method is one of the methods of covering an active material particle surface with lithium-ion-conductivity polymer of said solid state selectively. First, lithium salt is dissolved in the aforementioned resin which

heats and carried out melting, and the powder of polymer is produced by the method of drying, while injecting after cooling the method of grinding, or the solution in which aforementioned resin and lithium salt were dissolved in a hot wind, etc. Subsequently, an active material particle surface is covered if needed using this polymer powder with the powder of a conducting agent and a lithium-ion-conductivity inorganic solid electrolyte. Under the present circumstances, polymer powder covers an active material particle surface selectively, and the powder of a conducting agent and an inorganic solid electrolyte covers so that active material particle surfaces other than the portion covered with polymer powder may be covered selectively or extensively.

[0020]The method of putting in active material powder in a device with coating whose particle diameter is smaller than active material powder, i.e., polymer powder, polymer powder, the powder mixture of a conducting agent, or the powder that mixed inorganic solid electrolyte powder further, and performing coating treatment mechanically as [ both ] the coating method, is preferred. As the method of mechanical coating treatment, methods, such as the mechanical milling method by the hybridization method, the mechanofusion method, a planetary ball mill, a ball mill, etc., can be taken. Otherwise, methods, such as chemical coating processing which deposits polymer powder and a metal conducting agent in an active material particle surface, can also be taken by the unelectrolyzed composite plating in the inside of polymer powder and the dispersion liquid of a metal conducting agent.

[0021]As lithium-ion-conductivity polymer of this invention, To lithium-ion-conductivity polymer of the above-mentioned solid state, further Ethylene carbonate, Gel polymer containing organic solvents, such as polypropylene carbonate, ethyl methyl carbonate, dimethyl carbonate, and gamma-butyrolactone, or these mixed solvents can also be used. Since ionic conductivity is high, the gelled lithium-ion-conductivity polymer is much more effective in order to raise the high charging and discharging characteristic of a cell.

[0022]As a method of covering gel lithium-ion-conductivity polymer selectively to an active material particle surface, the following method can be taken, for example. First, an electrode is produced using the active material particle which covered lithium-ion-conductivity polymer of the solid state beforehand. That electrode is impregnated with the electrolyte which dissolved lithium salt in the organic solvent or the organic solvent, solid state polymer of an active material surface is dissolved in it, this is heated, and this polymer is made to gel by cooling.

[0023]At least one chosen from the group which consists of Ketchen black, acetylene black, black lead, metal powder, plastic powder that covered metal, and glass powder which covered metal as a conducting agent used by this invention is effective. As a lithium-ion-conductivity inorganic solid electrolyte,  $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ ,  $\text{Li}_{3.4}\text{V}_{0.6}\text{Si}_{0.4}\text{O}_4$ ,  $\text{LiTi}(\text{PO}_4)_3$ ,  $\text{LiPON}_x$  ( $0 < x \leq 1$ ) of amorphous nature,  $\text{LiX-Li}_2\text{S-Li}_2\text{O-P}_4\text{O}_{10-n}\text{S}_n$  (X is I or Br), etc. are effective.

[0024]As positive active material in this invention,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCo}_x\text{nickel}_{1-x}\text{O}_2$  ( $0 < x < 1$ ),  $\text{LiAl}_x\text{nickel}_{1-x}\text{O}_2$  ( $0 < x < 1$ ),  $\text{LiMn}_x\text{nickel}_{1-x}\text{O}_2$  ( $0 < x < 1$ ),  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  ( $0 < x < 1$ ), Metallic oxides, such as  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $0 < x < 1$ ),  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 < x < 1$ ),  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , and  $\text{NiOOH}$ , etc. can be used. at least one chosen from the group which consists of B, Na, Mg, aluminum, P, Ca, Ti, Cr, Fe, Cu, Zn, and Ga -- said metallic oxide -- 1 - 50at% -- the thing made to dissolve can also be used as positive active material.

[0025]As negative electrode active material in this invention, oxides, such as  $\text{Li}_{4/3}\text{Ti}_5\text{I}$  nitrides, such as charges of an alloy such as carbon materials, such as black lead in which the occlusion and discharge of lithium by charge and discharge are possible, a  $\text{TiSn}$  alloy, and a  $\text{TiSi}$  alloy, and  $\text{LiCoN}$ , or  $\text{I}_3\text{O}_4$ , can be used.

[0026]

[Example]Next, an example explains this invention concretely.

[0027]<<Example 1>> 5g of  $\text{LiClO}_4$  was dissolved into the solution which dissolved 30 g of polyethylene oxide in 600 ml of acetonitrile, and the lithium-ion-conductivity polymer solution was prepared. Next, it was made to dry and solidify, spraying this solution into a hot wind, and lithium-ion-conductivity polymer powder with a particle diameter of about 0.3 micrometer was produced. After fully mixing this powder 1g, the  $\text{LiCoO}_2$  powder 30g with a particle diameter of about 10 micrometers which is positive active material, and Al powder 0.2g with a particle diameter of 0.1 micrometer, the planetary ball mill performed coating treatment of the active material particle surface for 1 minute. This covered the surface of positive-active-material particles with lithium-ion-conductivity polymer powder and Al powder selectively.

[0028]The positive-active-material powder 10g after this coating treatment, 0.3 g of acetylene black, and the fluororesin powder 0.8g were fully mixed in acetone, and positive electrode paste was prepared. This positive

electrode paste was applied to the collecting electrode plate made from Al foil, after drying, it pressurized by the roll press, this was dried in a 60 °C vacuum, and the anode board was produced. This was pierced and processed and a disc-like anode 20 mm in diameter was produced.

[0029]Subsequently, after fully mixing the artificial graphite 20g with a mean particle diameter of 20 micrometers which is negative electrode active material, and the same lithium-ion-conductivity polymer powder 1g as the case where positive-active-material particles are covered, the ball mill performed coating treatment for 1 minute. This covered the surface of negative-electrode-active-material particles with lithium-ion-conductivity polymer powder selectively. The negative-electrode-active-material powder 10g after this coating treatment, 0.1 g of acetylene black, and the fluororesin powder 1g were fully mixed in acetone, and the negative-electrode paste was produced. This negative-electrode paste was applied on the charge collector made from Cu foil, after desiccation, it pressurized by the roll press and the negative electrode plate was produced. This negative electrode plate was dried in a 60 °C vacuum, it pierced to 21 mm in diameter disc-like, and the negative electrode was produced.

[0030]Next, after having laminated the anode, the separator, and the negative electrode, storing to the cell case made from stainless steel and pouring an electrolyte into this, the obturation board was made to fit into the opening of a cell case via a gasket, the crimp seal was performed, and the coin type cell was produced. The porous membrane made of polyolefin system resin of 25 micrometers of thickness was used for the separator. The organic electrolyte which dissolved 1 mol/L of  $\text{LiClO}_4$  in the solvent which mixed

ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:40:40 was used for the electrolyte.

[0031]<<Comparative example 1>> Positive-active-material particles and negative-electrode-active-material particles produced the coin type cell like Example 1 except not performing coating treatment.

[0032]The charge-and-discharge cycle test was done using the coin type cell of Example 1 and the comparative example 1. Charge-and-discharge temperature was 20 °C, constant current charge of current 0.2CA and the upper limit voltage 4.1V was performed, and constant current discharge of current 1CA and the final voltage 3.0V was performed. The number of charging and discharging cycles until service capacity turns into 70% of initial capacity was made into the cycle life. As a result, to the cycle lives of the comparative example 1 being 500 cycles, in Example 1, it is 680 cycles and the prominent effect of cycle-life Kougami of the cell

by this invention was accepted.

[0033]<<Example 2>> After adding 4g  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  to the acrylonitrile resin 30g, temperature up was carried out to 140 \*\*, melting of the above-mentioned resin was carried out, and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  was thoroughly melted in this resin.

Next, apply this fused resin on a glass substrate, cool, and it was made to solidify, and was made film state. This film was ground mechanically and lithium-ion-conductivity polymer powder with a particle diameter of about 0.3 micrometer was produced.

[0034]Next, after adding the above-mentioned lithium-ion-conductivity polymer powder 2g and the Ketchen black powder 0.4g with a particle diameter of 0.02 micrometer to  $\text{LiMn}_2\text{O}_4$  powder with a particle diameter of 15

micrometers which is positive active material and fully mixing, coating treatment for 2 minutes was performed by the mechanofusion method. This covered the surface of positive-active-material particles with lithium-ion-conductivity polymer powder and Ketchen black powder selectively. The anode was produced by the same method as Example 1 using the positive electrode paste which was fully mixed and prepared in acetone the positive active material 10g, and 0.3 g of acetylene black and the fluoro-resin 0.8g which performed this coating treatment.

[0035]Next, Ti powder 5g and the Sn powder 119g were mixed for ten days with the ball mill by a nitrogen atmosphere, and TiSn after alloy powder with a particle diameter of 15 micrometers was produced. Said after alloy powder 20g as negative electrode active material, the same lithium-ion-conductivity polymer powder 5g as having used for the coating treatment of positive-active-material particles, And after fully mixing the copper powder 0.2g with a particle diameter of 0.1 micrometer, coating treatment was performed for 5 minutes using the device for mechano fusions (the product made from Nara Machinery: Sita KOMPOZA). The negative electrode was produced by the same method as Example 1 using the negative-electrode-active-material powder which performed this coating treatment.

[0036]The coin type cell was produced like Example 1 using an above-mentioned anode and negative electrode. However, the organic electrolyte which dissolved 1.2 mol/l.  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  in the solvent which mixed ethylene

carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50 was used for the electrolyte.

[0037]<<Comparative example 2>> Positive-active-material particles and negative-electrode-active-material particles produced the coin type cell like Example 2 except not

performing coating treatment.

[0038]The charge-and-discharge cycle test was done by the same method as Example 1 using the coin type cell of Example 2 and the comparative example 2. To the cycle lives of the comparative example 2 being 50 cycles, in Example 2, it is 550 cycles and the result checked that the cycle life of a cell improved substantially by this invention.

[0039]<<Example 3>> LiNiO<sub>2</sub> 10g with a particle diameter

[ as positive active material ] of 12 micrometers, 0.3 g of acetylene black, and the fluoro-resin 0.8g were fully mixed in acetone, and positive electrode paste was prepared. The anode was produced by the same method as Example 1 using this positive electrode paste.

[0040]Next, the polymethacrylate resin 30g was dissolved in 600 ml of acetone, LiPF<sub>6</sub> 4g was dissolved in the solution,

and the lithium-ion-conductivity polymer solution was prepared. Lithium-ion-conductivity polymer powder with a particle diameter of about 0.3 micrometer was produced by the same method as Example 1 using this polymer solution. Acetone was volatilized mixing and stirring this polymer powder 2g, the LiCo<sub>3-x</sub>N<sub>x</sub> powder 10g as negative electrode active material, the SnO<sub>2</sub> powder 2g, and 0.5 g of acetylene black in acetone, and it dried in a 60 more \*\* vacuum. By the coating treatment of this negative-electrode-active-material particle, the surface produced the negative-electrode-active-material powder covered extensively by lithium-ion-conductivity polymer powder and a conducting agent. Next, the negative electrode was produced by the same method as Example 1 using the negative-electrode-active-material powder which performed this coating treatment.

[0041]The coin type cell was produced like Example 1 using an above-mentioned anode and negative electrode. However, the organic electrolyte which carried out 1 mol/l dissolution of the LiPF<sub>6</sub> was used for the solvent which

mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50 at the electrolyte.

[0042]<<Comparative example 3>> Positive-active-material particles and negative-electrode-active-material particles produced the coin type cell like Example 3 except not performing coating treatment.

[0043]The charge-and-discharge cycle test was done by the same method as Example 1 using the coin type cell of Example 3 and the comparative example 3. To the cycle lives of the comparative example 3 being 300 cycles, in Example 3, it is 600 cycles and the result checked that the cycle life of a cell improved substantially by this invention.

[0044]<<Example 4>> Except having used acetone as a solvent instead of acetonitrile, it is the same method as Example 1, and lithium-ion-conductivity polymer powder with a particle diameter of about 0.3 micrometer was produced. Next,  $\text{LiCo}_{0.5}\text{nickel}_{0.5}\text{O}_2$  10g with a particle diameter [ as this polymer powder 0.5g and positive active material ] of 10 micrometers, After mixing the with a particle diameter [ as a lithium-ion-conductivity inorganic solid electrolyte ] of 0.2 micrometer  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  powder 2g, and 0.3 g of acetylene black, coating treatment of positive-active-material particles was performed by the same method as Example 1. This covered selectively lithium-ion-conductivity polymer powder, the conducting agent, and the inorganic solid electrolyte on the surface of  $\text{LiCo}_{0.5}\text{nickel}_{0.5}\text{O}_2$  particles.

[0045]The positive-active-material particles 10g, 0.3 g of acetylene black, and the fluoro-resin 0.8g which performed this coating treatment were fully mixed in acetone, and positive electrode paste was produced. The anode was produced by the same method as Example 1 using this positive electrode paste. The negative electrode was produced by the same method as Example 1 as lithium salt added to lithium-ion-conductivity polymer except having used  $\text{LiPF}_6$  instead of  $\text{LiClO}_4$ .

[0046]An above-mentioned anode and negative electrode were pressurized via the inorganic solid electrolyte pellet, and unification molding was performed. This was stored to the cell case, the obturation board was fitted into the opening of a case via the gasket, and all the coin type solid lithium secondary batteries were produced by bending and obturating an opening. What carried out pressing of the  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  powder to disc-like [ 22 mm in diameter and 20 micrometers / in thickness ] was used for the electrolyte pellet.

[0047]<<Comparative example 4>> Positive-active-material particles and negative-electrode-active-material particles produced all the coin type solid lithium cells like Example 4 except not performing coating treatment.

[0048]The charge-and-discharge cycle test was done by the same method as Example 1 using the coin type cell of Example 4 and the comparative example 4. To the cycle lives of the comparative example 4 being 600 cycles, in Example 4, it is 1000 cycles and the result checked that the cycle life of a cell improved substantially by this invention. The ratio of the service capacity in the case of 2C discharge to the service capacity in the case of 1C discharge was 95% in Example 4, and was 40% in the comparative example 4. Thereby, the prominent effect of the improvement in a high

rate discharging characteristic by this invention was checked.

[0049]<<Example 5>> First, after fitting into a cell case, the temporary seal mouth of the obturation board is carried out loosely, the polymer powder of the active material particle surface was impregnated with the organic electrolyte, and this polymer was made to gel by heating this for 30 minutes at 70 °C in the obturation process at the time of producing a coin type cell. Final obturation was performed after that. The coin type cell was produced like Example 2 except this obturation process.

[0050]As a result of doing a charge-and-discharge cycle test by the same method as Example 1 using the coin type cell of Example 5, the cycle life of 750 cycles was acquired to 550 cycles of Example 2. Thereby, when it was gel rather than the ion-conductive polymer which covers an active material particle surface selectively is a solid state, it was checked that a cycle life improves more effectively.

[0051]

[Effect of the Invention]By this invention, the dimensional change of a lithium secondary battery and the increase of internal resistance by charge and discharge can be controlled effectively. A high rate discharging characteristic and a cycle life are substantially improvable.

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[Translation done.]